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NO_x FORMATION AND CONTROL DURING FOSSIL-FUEL COMBUSTION

Report No. 88-213-K

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ABSTRACT

The emission of NO_x into the atmosphere, as a result of the combustion of fossil fuels, is of concern because of its potential effect on the environment. A comprehensive survey of the available information on NO_x formation and destruction mechanisms during fossil-fuel combustion has been carried out. This information has been used to review the various methods available for NO_x reduction, including both in-furnace NO_x reduction techniques and flue gas treatments. Recommendations have been made regarding the best NO_x removal techniques to be used in various situations. Suggestions for research into possible future NO_x reduction techniques have been put forth.

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EXECUTIVE SUMMARY

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The emission of NO_x (NO and NO_2) into the atmosphere, as a result of fossil-fuel combustion, is of concern because of its potential effect on the environment through acid rain and through its role in ozone formation and the subsequent effects on vegetation. In view of this, a comprehensive survey of the available information on the various NO_x formation and destruction mechanisms occurring during fossil-fuel combustion has been carried out. This information has been used to review the methods available for NO_x reduction, including both in-furnace NO_x removal techniques and flue gas treatments. Combustion modification techniques have been found to provide the simplest and most economical method of control when conditions allow for their use and when only a moderate NO_x removal efficiency is required. Flue gas treatments are more efficient means of reducing NO_x emissions, especially for existing facilities, since combustion modification is not highly effective in retrofit situations. The most efficient flue gas treatment technique is selective catalytic reduction. Other methods of lower efficiency or greater technical complexity have been described as well. Suggestions for research into possible future NO_x reduction techniques have also been put forth.

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To Dr. D. Mills
Director of Research

NO_x FORMATION AND CONTROL DURING FOSSIL-FUEL COMBUSTION

1.0 INTRODUCTION

The problem of nitrogen oxides in the atmosphere has begun to be of more concern to environmental control agencies in North America over the last few years (Hakkarinen, 1987). Although the effects are not yet well understood, it is now quite strongly felt that nitrogen oxides (NO_x) may be almost as much of an environmental hazard as is sulfur dioxide (SO_2).

The term NO_x is normally considered to represent a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2). In the stack gases, NO can be converted to N_2O. When exposed to the atmosphere, NO_x species are precursors, through atmospheric reactions, for other nitrogenous species such as nitric acid (HNO_3), and peroxyacetyl nitrate (PAN). These subsequent species are thought to cause other problems. Nitric acid plays a large role in acid rain; reaction of NO in the troposphere generates ozone which is implicated in vegetation destruction and health effects; N_2O has an effect on world climate (Tirpak, 1987); and the ozone layer. Formation of these subsequent species cannot be prevented since their formation is the only means of removal of NO and NO_2 from the atmosphere other than through dry deposition processes. The control of such nitrogenous species must therefore begin at the source as control of NO and NO_2.

It was once thought that automobile emissions were the major source of atmospheric NO_x. Now that emission controls have been installed on automobile engines, the problem with NO_x emissions from power generating stations which burn fossil fuels, particularly coal has become of more concern. The control of NO_x from power plants has been pursued vigorously in some countries, Japan and West Germany in particular. Regulations governing NO_x emissions from stationary sources have been

drastically tightened and as a result many research and technology advances have been made into the reduction of these emissions. Many reviews of these advances are in the literature (eg, Ando et al, 1977; Glass et al, 1983).

Current regulations for NO_x emissions in Canada are quite lenient compared to those in Japan and West Germany. It is a distinct possibility that they could be severely tightened in the foreseeable future. This concern suggests that consideration of the methods of NO_x control should occur within Ontario Hydro. The purpose of this report is to address these matters.

For the case of thermal generating plants, NO is practically the sole nitrogen oxide of concern. It is estimated that at least 95% of the nitrogen oxides leaving the generating plant stack are in the form of NO (Merryman and Levy, 1974). It is not until emission into the atmosphere that NO and NO_2 come into equilibrium through the $NO-O_3-NO_2$ photochemical cycle.

This report will review what is known about the formation of NO in the combustion processes of thermal generating stations. The mechanisms of formation will be examined with a view toward ways of reducing this formation. Beyond the combustion process, the currently used and previously attempted methods for removal of this NO will be examined. Recommendations of the best available technology will be made as will suggestions for areas of further research where Ontario Hydro might make a contribution to the field.

2.0 NO_x FORMATION IN COMBUSTION PROCESSES

Before one can begin to deal with the prevention of NO formation in combustion processes, it is necessary to have a detailed understanding of the mechanisms of this formation and of the parameters which affect these mechanisms. There has been a great deal of research done over the past twenty years to determine the mechanisms of the various processes involved in NO formation. The progress has been slow but steady in filling in the gaps between pieces of information to the point where the mechanisms are currently quite well understood although some information is still missing.

All of the NO formed during combustion of fossil fuels is formed in the relatively high temperature regions of the furnace ($T > 1500°C$). Beyond this point, the concentration of NO formed in the high T region remains constant and will appear in the exhaust gases unless some subsequent steps are taken to remove it. This section of the report will attempt to explain what is known about the processes leading to this concentration.

There are three basic formation mechanisms for NO in the high temperature regions of the furnace (Barnard and Bradley, 1985; Bergsma, 1985). These are described as "thermal NO_x" formed from the thermal fixation of atmospheric nitrogen (Zeldovich, 1984; Thompson et al, 1973), "prompt NO_x" from the reaction of fuel hydrocarbon radicals with molecular nitrogen (Fenimore, 1971; Blauwens et al, 1979; Hayhurst and Vince, 1983), and "fuel NO_x" formed from the combustion of nitrogeneous compounds in the fuel itself (Appleton and Heywood, 1973; Pershing and Wendt, 1979; Okazaki et al, 1984; Kruger et al, 1987). These are considered to be three independent formation mechanisms which have no effect on one another (Bergsma, 1985). As a result they will be discussed independently.

As the name suggests, thermal NO_x is the result of a reaction driven by high temperature, the overall endothermic reaction of molecular nitrogen with molecular oxygen:

$$N_2 + O_2 \longleftrightarrow 2NO \qquad (1)$$

This reaction proceeds through a chain reaction via the extended Zeldovich mechanism (Zeldovich, 1946; Bergsma, 1985):

$$N_2 + O \longleftrightarrow NO + N \qquad (2)$$

$$N + O_2 \longleftrightarrow NO + O \qquad (3)$$

$$N + OH \longleftrightarrow NO + H \qquad (4)$$

This is an equilibrium-driven reaction system initiated by the high temperature equilibrium of oxygen atoms with molecular oxygen:

$$O_2 + M \longleftrightarrow O + O + M \qquad (5)$$

The chain reaction propagates by maintaining the radical concentration produced by reaction 5 until chain terminating steps are reached or until the temperature drops too low to allow the rate limiting reaction 2 to occur. The barrier for reaction 2 is 303 kJ mol^{-1} (Fenimore, 1971). The reaction set need only contain reactions 2,3 and 5 to proceed. Reaction 4 is included to allow for the possibility of other components in the system (eg, H_2O) playing a role in the radical formation mechanism (Fenimore, 1971).

Because of the high endothermicity of thermal NO formation, it is only important at temperatures above 1800 K (Acree and LaRue, 1985). As a result it only takes place in the combustion gases just beyond the flame where the hottest temperatures are reached (Merryman and Levy, 1974) and where therefore the greatest concentration of radicals is seen. Only a small amount of thermal NO_x has ever been seen to be formed in the flame itself.

With the mechanism for formation of thermal NO_x defined, a number of parameters can be seen to affect it (eg, Bergsma, 1985; Pohl et al, 1987). Table 1 shows some of them. Reducing the temperature in the furnace will reduce the formation of thermal NO_x due to the endothermicity of the process. Reducing the radical concentration by some sort of scavenging process will have a similar effect. For example, under conditions where the fuel concentration is in excess of the oxygen concentration, the O atoms will preferentially react with the hydrocarbons. The third parameter affecting the amount of thermal NO_x formation is the residence time in the high temperature zone of the furnace. Since the Zeldovich mechanism depends on an equilibrium situation, reducing the residence time will reduce the degree of equilibrium reached. The extent to which these parameters can be varied to achieve reduced NO formation will be discussed in subsequent sections of this report.

The relative contribution of thermal NO formation to the total amount of NO produced depends on the fuel used and its nitrogen content. In general, for coal-fired furnaces the contribution of the "thermal" mechanism is thought to be less than 20% of the total (Pohl et al, 1987).

A second mechanism proposed for NO produced from thermal homogeneous reaction in the high temperature region of the furnace is the so-called "prompt NO" formation mechanism Fenimore, 1971; Blauwens et al, 1979; Hayhurst and Vince, 1983). This is a series of reactions of hydrocarbon radicals with molecular nitrogen to form compounds which react quickly with oxygen to form NO. This mechanism was originally put forth to account for the fact that a higher concentration of non-fuel NO was produced than could be attributed to the Zeldovich mechanism (Fenimore, 1971). In addition this mechanism produced NO in the flame rather than in the post-flame gases where thermal NO appears (Blauwens et al, 1979). There was initially much controversy about the source of this NO, but sufficient evidence now exists to support the hydrocarbon radical mechanism.

The prompt NO mechanism is thought to proceed via the production of HCN from the reactions of molecular nitrogen with a variety of hydrocarbon radicals - predominantly CH and CH_2 (Blauwens et al, 1979):

The HCN produced in this way can then react rapidly with oxygen or with the hydroxyl radical (OH) to ultimately produce NO (Hayhurst and Vince, 1983). Hydrocarbon radicals, other than CH and CH_2, could play a role in this mechanism, but their lower concentrations will make the contribution quite small.

TABLE 1

EFFECT OF VARIOUS PARAMETERS ON NO FORMATION

Parameter	Effect		
	Thermal NO	Prompt NO	Fuel NO
Temperature	up	up	no effect
Residence time	up	?[a]	?[a]
Oxygen concentration	up	down	up
Radical concentration	up	?[a]	?[a]
Fuel nitrogen	NA[b]	NA[b]	up

[a] - a question mark indicates that both NO formation and destruction mechanisms exist and this parameter could therefore produce any effect on the NO emitted depending on the other conditions.

[b] - NA means that this parameter is not applicable to this NO formation mechanism.

$$CH + N_2 \longrightarrow HCN + N \qquad (6)$$

$$CH_2 + N_2 \longrightarrow HCN + NH \qquad (7)$$

The formation of prompt NO depends on temperature and occurs mostly in the region of 1900-2400 K in the flame (Bergsma, 1985) where the concentration of hydrocarbon radicals is high. Since this formation proceeds via hydrocarbon reaction, it is obvious that the mechanism is predominantly active under fuel-rich conditions. In general, one expects that higher fuel concentrations will yield more NO via the prompt formation mechanism. As will be discussed later however, this is not true for very fuel-rich conditions since there exists a mechanism for the destruction of NO by hydrocarbon radicals as well (Hayhurst and Vince, 1983). As a result, the prompt NO formed is usually only a small contribution to the total NO, but it must be considered as a lower limit for NO production when no fuel NO is produced.

As shown in Table 1, one can hope to reduce the formation of prompt NO in much the same ways as for thermal NO. That is, a reduction in combustion temperature or a reduction in residence time of the gases in the high temperature regions will result in less NO formation. In contrast to the thermal mechanism, however, a reduction in oxygen availability will likely increase the prompt formation since oxygen serves as a route to scavenge hydrocarbon radicals (Bergsma, 1985).

For solid and liquid fossil fuels, by far the largest portion of NO is formed through the combustion of nitrogen containing compounds which are bound in the fuel itself (Pershing and Wendt, 1979). The amount of fuel nitrogen varies strongly with the type of fuel used. Fuel nitrogen content increases from gaseous fuels to liquid fuels to solid fuels (Okazaki et al, 1984). This discussion will deal predominantly with solid fuels - coal to be specific - since this is of most interest to Ontario Hydro.

Even within a particular category of fuels, the amount of fuel NO produced by combustion will vary extensively. The nitrogen content of coal ranges from 0.2% by mass to greater than 2% (Bergsma, 1985). The amount of NO produced from this nitrogen will depend on a variety of factors including how the N is bound in the coal. Nitrogen is commonly found in coal bound in N-heterocyclic compounds such as pyridines, quinolines, pyroles, indoles and carbazoles (Appleton and Heywood, 1973). The type of compounds will determine how much is readily released and in what form.

Although much research has been done into production of fuel NO, not all of the details of the mechanism are known. There is enough information, however, to postulate a mechanism which is adequate to describe the situation. It is well known that the path from fuel nitrogen to NO leads through a HCN intermediate (Song et al, 1981), but exactly how the HCN is initially formed is not completely clear. There is a problem in obtaining more information about this process because it is such a fast, exothermic process at combustion temperatures (Appleton and Heywood, 1973). This is the expected situation because the C--N heterocycle bonds are considerably weaker than the 225 kcal mol^{-1} bond in molecular nitrogen and are therefore much more readily broken. It is assumed that pyrolysis during the combustion process begins by ring cleavage at the C--N heterocycle bond followed by breakup of the rest of the molecule and the ultimate formation of HCN (Song et al, 1981). HCN is then treated as the effective initial gas phase species in the fuel-rich combustion to form NO. It is certainly the gaseous nitrogen-containing compound which has been detected earliest in the flame (Song et al, 1981).

Once formed, HCN is rapidly converted to amine-type species (NH_i, i=0-3) which will undergo further reaction to produce either NO or N_2 (Blair et al, 1979; Pohl and Sarofim, 1979):

$$\text{fuel-N} \longrightarrow \text{HCN} \longrightarrow NH_i \quad (i=0-3) \tag{8}$$

$$NH_i + O,OH \longrightarrow NO \tag{9}$$

$$NH_i + NH_i, NO \longrightarrow N_2 \tag{10}$$

One of the major reactions contributing to NO formation is thought to be:

$$N + OH \longrightarrow NO + H \tag{11}$$

especially for fuel-rich conditions. Obviously, the crucial factor in reducing the amount of NO formed from the fuel-N is to maximize the N_2 formation branch of the amino radical reaction scheme, equation 10.

To consider the problem of fuel NO formation, one must have some comprehension of what parameters affect the production of HCN from the nitrogen in the fuel. This conversion depends on a variety of parameters, all basically determined by the amount of volatile nitrogen containing material in the coal (Blair et al, 1979). The amount of volatile material will vary strongly from coal to coal. Any material which is not volatile is going to remain in the char left after the main combustion zone. While it appears that this nitrogeneous material will not give rise to NO, allowing this material to go unburned makes for a very inefficient use of the energy available in the fuel. This necessitates the use of a secondary combustion area to burn the char material, at which point the rest of the nitrogeneous material can be released as NO. The efficiency of NO production will differ between the primary and secondary combustion processes and it is fortunate that the secondary combustion is usually less efficient at forming NO (Pershing and Wendt, 1979).

The fraction of nitrogen-containing material that is devolatilized depends on a variety of parameters (Blair et al, 1979; Pohl and Sarofim, 1979). These include: (i) the form of nitrogen in the coal; (ii) the coal particle size, (iii) the flame temperature, (iv) the heating rate of the coal particles; (v) the fuel richness of the combustion mixture and (vi) the residence time in the flame which is determined by the flow rates as well as the overall size of the flame. While these parameters are important for determining the amount of volatile nitrogeneous material that is released, some of them are not all that important in determining the amount of NO produced since the remainder of the nitrogeneous material must be combusted eventually, to achieve efficient energy production.

The extent to which fuel-N becomes NO can be controlled through a variety of parameters (see Table 1). The most obvious parameter is the N content of the fuel. Attempts have been made to reduce the N content of the fuel, but they have met with little success (Ando et al, 1977). In any event, it has been found that when the nitrogen content is very high there are mechanisms available to provide self-destruction of the NO formed. This will be discussed in the next section. The most successful way to prevent NO formation is to limit the oxygen that is available for reaction (Ando et al, 1977; Eliot, 1978). Under fuel-rich conditions, one is dealing with an environment which is overall reducing rather than oxidizing, leading to the amino radicals preferentially being reduced to N_2 (equation 10) rather than oxidized to NO (equation 9). It should be noted that unlike the production of thermal and prompt NO, the formation of fuel NO does not depend on the amount of molecular nitrogen that is available (Fenimore, 1972).

The remaining controllable parameters are the flame temperature and the residence time in the flame. It has been shown that the amount of fuel NO formed is essentially independent of temperature. This is predominantly because, as discussed above, most of the nitrogen containing material has to be combusted eventually and the highly volatile material comes off very easily. Residence time in the flame is a bit more complicated since there are also NO destruction mechanisms in the flame.

Since the fuel NO channel accounts for 70-80% of the NO formed during the combustion of coal, most of the work done toward limiting NO formation has addressed this formation mechanism. This will become more evident during the following discussion.

3.0 NO DESTRUCTION MECHANISMS IN COMBUSTION PROCESSES

The previous discussion seems to suggest that there is a strong tendency to form NO from combustion processes involving nitrogeneous compounds. The situation is not that bleak, however, since there are natural mechanisms in the flame for the destruction of NO as well as for its formation (Song et al, 1981; Acree and LaRue, 1985; Bergsma, 1985). As a result, an understanding of these mechanisms will help in establishing conditions which promote the destruction of NO and therefore allow for a much lower overall release of NO in the exhaust gases.

As mentioned previously, there are hydrocarbon radical reactions for reducing NO, as well as the reactions that exist for producing it. These reactions again primarily involve reactions of CH and CH_2 (Song et al, 1981):

$$CH + NO \longrightarrow CN + OH \quad (12a)$$

$$\longrightarrow HCN + O \quad (12b)$$

$$\longrightarrow HCO + N \quad (12c)$$

$$CH_2 + NO \longrightarrow N + CH_2O \quad (13a)$$

$$\longrightarrow HCN + OH \quad (13b)$$

It is evident that under the proper fuel-rich conditions these NO destruction reactions may play a larger role. It should be noticed that NO, which was originally formed from HCN, is recycled back through HCN by some of these reactions. Since only a portion of the HCN becomes NO (the rest reacts to give N_2), a greater extent of recycling will ultimately result in a lower emission of NO (Kramlich et al, 1987).

This mechanism for NO destruction can be taken advantage of by the use of a reburning mechanism whereby post-combustion gases are recirculated into the flame or where additional hydrocarbon radicals are generated by means of a secondary fuel injection process.

Most evidence suggests that during fuel-rich combustion the destruction of NO is dominated by gas phase reactions (Glass and Wendt, 1982). The above reactions are part of this, but by far the largest contributors to NO destruction are the reactions of amino radicals (NH_i, i=0-2) to reduce NO (Song et al, 1981; Song and Bartok, 1982).

$$NH_2 + NO \longrightarrow N_2 + H_2O \quad (14)$$

$$NH + NO \longrightarrow N_2 + OH \quad (15)$$

$$N + NO \longrightarrow N_2 + O \quad (16)$$

All of these reactions are exothermic and very fast (Morley, 1981). As a result, under fuel-rich conditions, where the formation of HCN leads to a higher concentration of the amino radicals, the probability of these destruction reactions occurring is very high. Therefore, in addition to allowing fewer O and OH radicals to produce NO, the fuel-rich conditions, under a sufficiently long residence time have the double effect of removing some of the NO which was formed.

While it is not yet well understood which of the amino radical reactions dominates the NO destruction mechanism, some guidelines are available. It is well known that the NH_2 radicals are kept in a constant state of equilibrium by: (Morley, 1981).

$$NH_i + H \longleftrightarrow NH_{i-1} + H_2 \quad (17)$$

As a result, under conditions where the radical concentration is low, the NO destruction will be dominated by NH_2 (equation 14) and when the radical concentration is high, the dominant reaction will involve the N atom (equation 16).

It should be noted that for some of these NH_i reactions there are other branches which can lead to N_2O formation (Whyte and Phillips, 1983; Harrison et al, 1986):

$$NH + NO \longrightarrow N_2O + H \quad (18)$$

$$NH_2 + NO \longrightarrow N_2O + H_2 \quad (19)$$

Branching ratios that have been measured for these reactions would suggest that the N_2 product channel dominates with N_2O being formed only to a small extent (Mulvihill and Phillips, 1975; Silver and Kolb, 1982). This must be taken into consideration, however, in view of the contribution of N_2O to the global greenhouse effect (Tirpak, 1987).

Under some conditions there is a further set of reactions leading to the destruction of NO through heterogeneous reaction (Levy et al, 1981). These reactions involve the char left unburned from the combustion process. There are possible direct reactions of NO with the char:

$$2NO + 2C \longrightarrow 2CO + N_2 \quad (20)$$

$$2NO + C \longrightarrow CO_2 + N_2 \quad (21)$$

as well as char-catalyzed reaction of NO with CO:

$$2NO + 2CO + \text{char} \longrightarrow N_2 + 2CO_2 + \text{char} \quad (22)$$

While these reactions are thought to occur to some extent, there are problems with O_2 interference (Levy et al, 1981). Oxygen, in much higher concentration than NO, reacts very quickly with the char depleting it rapidly. There is also a mechanism for atomic oxygen to chemisorb on the char surface thereby blocking the catalytic reaction. The char NO destruction reactions are best taken advantage of in areas where the temperature remains high (>800°C) and the oxygen concentration remains low (Acree and LaRue, 1985).

With these three families of reactions (hydrocarbon radicals, amino radicals, heterogeneous char production) available to destroy NO during and after the combustion process, it would seem that it should be possible to optimize the combustion conditions to take advantage of this and limit the emitted NO to a low concentration. Problems arise, however, because of the inability to accurately model the set of reactions producing and destroying NO (Kramlich et al, 1987). There are just too many variable parameters and too little control of them in practice.

The next section will describe some of the attempts made to take advantage of this information to minimize NO emission by combustion modification techniques.

4.0 IN-FURNACE NO_x CONTROL TECHNIQUES

4.1 Combustion Modification Methods

The easiest and best way to deal with NO emission from thermal generating stations is to attempt to eliminate its initial formation during the combustion process, rather than attempting to remove it from the flue gas. For this reason, there has been a great deal of research done into combustion modification techniques to find a method of combustion which produces only low levels of NO emissions (eg, Ando et al, 1977, Pruce, 1981, Glass et al, 1983, Acree and LaRue, 1985).

One should recall from the discussion of NO formation that there are a variety of parameters that can be varied to change the amount of NO emitted. These parameters include burner temperature, fuel-richness of the flame, residence time in the high temperature region and the type of fuel. When considering combustion modification, one must bear in mind that there will likely be a lower limit in the NO produced because of the balance that must be established between thermal NO, prompt NO and fuel NO and between the amount of volatile fuel NO produced and the amount of char NO produced.

Staged combustion is the most common way of modifying the combustion process in coal-fired boilers (Acree and LaRue, 1985). It involves adding the amount of air needed for complete combustion of the fuel in two or more stages thereby allowing the combustion mixture to be fuel rich when necessary for NO reduction and air rich when necessary to complete the combustion process. This allows a proper balance between temperature and fuel-richness to optimize conditions in all combustion zones for overall minimum NO formation and maximum energy production.

The main combustion zone is operated under very fuel rich conditions at high temperatures (Acree and LaRue, 1985) which favour the conversion of fuel-N to N_2 rather than NO. It is important to maximize the residence time in this zone to both maximize fuel consumption under limited oxygen conditions and to take advantage of NO reduction reactions with both hydrocarbon radicals and amino radicals as discussed in the previous section.

There must be at least one other combustion zone to provide a region for completing the combustion process on any unburned fuel leaving the primary combustion zone. This will be a fuel lean zone from the point of view of allowing the excess air to maximize combustion. One must still be careful to keep the

oxygen content and the temperature as low as possible as there will still be fuel-N remaining in the char which is readily converted to NO during this combustion stage and will not be subsequently reduced. It is also possible to add intermediate combustion zones to help to complete the combustion process under more fuel rich conditions. This is done in the distributed mixing burners of Dutch design which produce quite low NO emissions (Glass et al, 1983).

Another method of combustion modification is achieved by adding a reburning stage after the primary combustion zone to take advantage of hydrocarbon radical reactions to reduce the NO that was formed in the primary zone (Bortz and Offen, 1987; Pershing, 1987). This technique could be referred to as "fuel staging." This can be done by reserving some of the fuel for injection beyond the primary zone. This technique is not as effective for coal-fired burners as for other fuels because of the large N content of coal providing a large source of NO that can now be released in the reburning zone. The same effect can also be achieved by injecting a secondary fuel (other than coal) into the reburning zone. Natural gas is preferred for this since it is a very clean gas in terms of nitrogen content (Bartok et al, 1987).

These methods describe what is required in terms of combustion modification to reduce the amount of NO formed. In order to actually put this into practice, a great deal of engineering and design has been required to achieve the desired results (eg, Ando et al, 1977; Glass et al, 1983; Acree and LaRue, 1985). Drastic improvements have been required in burner design and in the entire furnace design as well since one must be concerned with the temperature and mixing properties of the various combustion zones.

There have been many different designs put forth for burners, all of which work on the same basic staged combustion principle (Clark et al, 1987; Kiga et al, 1987). One can achieve the air staging either internally by diverting the air flow from the flame region or externally by making use of injection ports outside the main burners. A common technique has been to do this by adding overfire air above the main burner region (Smith et al, 1982; Lisauskas et al, 1987). Regardless of the method employed for air staging, one must be very concerned with the mixing and flow criteria for the complete furnace. It is very important that the air from one combustion stage does not mix with that from another zone or the staging effect will be lost. On the other hand, good mixing conditions and turbulence are required within each combustion zone to maximize the residence time under the desired conditions. This can pose complicated engineering problems.

Other problems can result from combustion modification as a result of the very corrosive atmosphere that can arise from the products of the various stages. Slagging can produce deposits on the burner walls because of the reducing atmosphere that is present in the primary combustion zones (Kiga et al, 1987). This problem can only be overcome by producing an oxidizing atmosphere near the walls by the injection of higher air concentrations in these areas. If precautions are not taken to avoid these situations, serious boiler damage can result.

Engineering consideration must also be given to the flame itself since flame shape can have a large effect on the combustion process (Clark et al, 1987). A longer flame means a longer residence time in the high temperature fuel rich zone and therefore a lower emission of NO from the primary combustion zone. The lowest overall NO emission results from minimizing the primary zone emissions.

The other major problem that can result is that of reduced energy production because of incomplete combustion. It is very important to determine what level of burnout (lack of combustion) can be tolerated and design the burner around this parameter. A burnout level of <5% is normally chosen (Kiga et al, 1987). As a result, if the primary combustion zone is not efficient enough it may produce low NO, but much higher concentrations of NO are then emitted when the char is burned in subsequent fuel lean stages.

To deal with these problems, a great deal of research and development has gone into combustion during the past 10-15 years with a great deal of success (eg, Crawford et al, 1974; Ando et al, 1977; Eskinazi, 1985). The Japanese have been the leaders in this field to the point where they are now claiming operating burner designs which produce on the order of 200 ppm NO from high nitrogen content coals (Kiga et al, 1987). The European and American designs are moving toward similar results (Clark et al, 1987). As a result many manufacturers have very good burners on the market.

Despite the success achieved in burner design, there are still problems in putting these combustion modifications into practice. It is difficult to predict how well a particular design will perform for a particular coal. The success in NO reduction obviously depends greatly on the coal properties in that one must be aware of how much of the coal is composed of volatile material and how much of it is going to remain as char outside the primary stage of combustion. The burner is normally designed around this parameter to produce the lowest possible NO emission. As a result one cannot achieve the same lower limit of NO for different coals using the same burner

conditions (Pershing and Wendt, 1979; Chen et al, 1982; Kiga et al, 1987). A change in the coal usually burned can therefore lead to a drastic change in the NO emission properties of the boiler.

There are significant efforts being put into models to predict the effect of different coals on various burner designs, but the success has not yet reached the level required for reliable predictions (Lisauskas et al, 1987). The modelling process involves a very complex array of parameters of combustion properties and coal properties.

One of the real problems standing in the way of successful widespread use of combustion modification is in the area of retrofits to existing furnace designs (Clark et al, 1987). While entirely new burners are performing very well, modifications to existing apparatus are not meeting with the same low NO production results. Some success has been achieved in this area with about a 50% reduction in NO achieved for retrofit designs to existing burners. This can still leave NO emission at levels on the order of 400 ppm for these furnaces. Space limitations can create severe problems in implementing combustion modifications to existing facilities. It is thought that the optimum retrofit performance may already have been met necessitating complete replacement of existing furnaces if more stringent NO controls must be met using only combustion modification procedures. Flue gas NO removal techniques can be applied in addition to combustion modification to avoid this situation.

4.2 Furnace Additives

While combustion modification techniques have been the most common in-furnace NO reduction methods, there have been attempts to achieve additional in-furnace NO reduction through the use of additives. Generally, this has involved secondary fuel injection as described briefly in the previous section. Attempts at steam injection have also been made.

As mentioned previously, in the case of secondary fuel injection it is important to choose a fuel which is low in nitrogen content. Natural gas is normally the fuel of choice since it is a very clean fuel (Wendt et al, 1972; Bortz and Offen, 1987). It is also very easily dispersed which helps in NO reduction as a result of the good mixing in the secondary fuel combustion zone. Natural gas also has the advantage of being much more easily pyrolyzed than other fuels thereby requiring less residence time for this combustion stage. While secondary injection of natural gas does work for the reduction of NO, it is a costly system to implement. This is mostly due to the excess cost of the natural gas, an expensive fuel. To avoid this additional expense, many manufacturers seem to suggest that the proper choice of air staging conditions can result in the

emission of lower NO concentrations than those that can be achieved through the use of a secondary reburning fuel (Kiga et al, 1987).

The injection of steam into the furnace has also shown some reduction in the amount of NO emitted (Miyauchi et al, 1981). Only small reductions have been obtained, however, for additions of steam up to 10 mol per cent of the combustion mixture. The reductions that are achieved occur because of an increased radical concentration. The presence of water vapour increases the availability of O and OH radicals through equilibrium reactions:

$$O + H_2O \longleftrightarrow OH + OH \qquad (23)$$

$$H + H_2O \longleftrightarrow H_2 + OH \qquad (24)$$

Additional problems can arise with steam injection in view of the fact that the major effect is to reduce the flame temperature. This necessitates extra heating of the area to maintain combustion efficiency. As a result, steam injection appears not to be a highly efficient means of reducing NO emissions.

5.0 FLUE GAS TREATMENT

While it is preferable to remove as much of the NO as possible at the source through combustion modification, the previous discussions have shown that it is not always possible to achieve the desired results. There is a lower limit on the NO emissions that can be achieved through combustion modification and under very strict NO control regulations this might not be good enough. This is currently the situation in Japan (Ando et al, 1977). The additional problems of varying performance with the choice of coal and the retrofit problems have suggested that other alternatives should be available.

The alternative methods of NO reduction involve treatment of the flue gases as has generaly been the practice with SO_2 removal. These techniques are necessarily going to be more expensive and less convenient to use in most situations. A wide variety of flue gas treatment techniques have been tried over the years (eg, Ando et al, 1977; Glass et al, 1982; Eskinazi, 1985). A survey of them will be presented here with detailed descriptions given for the more successful and more widely used methods. Wet treatments and dry treatments will be dealt with separately.

5.1 Wet Flue Gas Treatments

Many types of wet flue gas NO_x removal treatments have been tried and they are reviewed in a variety of sources (Ando et al, 1977; Glass et al, 1983; Harkness and Doctor, 1985). The popularity of wet treatments has arisen because of the success

of some of these treatments in removing SO_2 from flue gases. It was thought that a method of simultaneous NO and SO_2 removal might be found. This might be possible depending on the extent of NO removal that is required but there are complications in using wet processes for NO flue gas treatment, as for SO_2 removal.

In general, wet treatments tend to be based on processes that are chemically more complicated than most dry processes. This leads to more parameters that must be controlled during the treatment. It also usually leads to a waste liquor (eg, HNO_3) or waste solid (eg, nitrates) resulting from the removal process (Ando et al, 1977). This problem has already been encountered with SO_2 removal and in many cases, a useful product can be obtained. One must still be prepared to collect this product and remove it from the stack, or treat it to make a more usable or less harmful product. Many of the products are quite corrosive.

A major problem in using wet treatments to remove NO results from the low solubility of NO in solution (Harkness and Doctor, 1985). Most of the currently used techniques involve absorption of the pollutant species (SO_2 or NO) in solution followed by its reaction with another species in the solution. Because of the low solubility of NO, it must first be oxidized to the more soluble NO_2 to allow the use of smaller volumes of the treatment solution. This adds a further complication to the process and also increases the cost of the process through the need for oxidizing species (eg, O_3, ClO_2) (Richards and Fox, 1980). Complications can also arise from the possible interference between NO and SO_2 removal in attempts to carry out a simultaneous removal process (Ando et al, 1977).

Several simultaneous wet treatments have met with some success (Glass et al, 1983). One of these is the SULF-X process which makes use of a wet slurry of FeS as the reagent and reacts with NO directly to produce N_2:

$$NO + Fe^{+2} \longrightarrow Fe(NO)^{+2} \qquad (25)$$

$$HSO_3^- + Fe(NO)^{+2} \longrightarrow Fe^{+2} + H^+ \; SO_4^{-2} + 1/2 \; N_2 \qquad (26)$$

This is a useful process in that it has the possibility of removing NO as N_2 rather than in a solid or liquid byproduct. While it does work to some extent, the efficiency for NO depends on the contact time that is available between the flue gas and the slurry, therefore necessitating large volumes to achieve much removal. The ammonia scrubbing process of CEC (Chesso Engineering Co. Ltd., Tokyo), which makes use of a soluble catalyst shows only limited success for NO although it works well for SO_2. Several other processes have also been

developed by the Japanese with either limited success for NO removal or problems with the byproducts or SO_2 interference (Ando et al, 1977).

Much work has recently been carried out at Argonne National Laboratory to study joint NO/SO_2 removal techniques (Harkness and Doctor, 1985). They have achieved some success by adding chelating agents to the standard SO_2 treatment solutions. The most successful additive has been found to be Fe-EDTA, which has been used previously by others (Ando et al, 1977). They have used this with a variety of SO_2 removal processes (lime, citrate, etc) but have achieved the most success with its addition to the dual alkali process, obtaining up to 60% removal for low (50 ppm) initial concentrations. This process works by absorbing HNO_2 in solution, as a result of a reaction between NO and NO_2 to give N_2O_3 which reacts with water to give HNO_2.

While some success has been seen in the benchscale experiments, there have been a variety of problems associated with the Argonne NO removal technique. It is a very pH sensitive process so that proper control of conditions must be maintained. One of the major problems can arise because of oxygen interference. O_2 oxidizes Fe^{+2} to Fe^{+3} which does not react with NO. There was no interference problem encountered with SO_2 removal. In fact, the presence of SO_2 seemed to have a helpful effect on the NO removal. There is also the additional problem that the NO is removed through the formation of hydroxylamine-N-sulfonates which must be dealt with. The authors feel that in general, technical problems will limit the practical effectiveness of such a process to less than 50% NO removal, under optimized conditions.

5.2 Dry Flue Gas Treatment

Dry methods of flue gas treatment have been far more popular than wet treatments for NO removal. Their chemical simplicity, as well as the fact that they normally produce N_2 as a harmless gaseous product have caused this. In addition, they are generally cleaner systems than wet processes and are in some cases less costly, at least on the surface. The most successful dry treatment processes have been the Exxon thermal $DeNO_x$ process, and processes of this type, and the Japanese selective catalytic reduction method. These techniques will be discussed in detail and other processes will be briefly mentioned.

5.2.1 Exxon Thermal $DeNO_x$ Process

There has been a great deal of research done into ways of taking advantage of the amine-type radical reactions discussed in Section 3.0, to reduce NO to N_2 in lower temperature regions outside the combustion area (Perry and Siebers, 1986; Lyon and Hard, 1986; Lyon, 1987; Mansour et al, 1987). There has also

been a lot of fundamental study into the kinetics (Gehring et al, 1973; Andersen et al, 1982; Silver and Kolb, 1982; Whyte and Phillips, 1982; Harrison et al, 1986) and dynamics of these reactions (Dreier and Wolfrum, 1984):

$$NH_3 + NO \longrightarrow NH_2 + HNO \quad (27)$$

$$NH_2 + NO \longrightarrow N_2 + H_2O \quad (14)$$

$$NH + NO \longrightarrow N_2 + OH \quad (15)$$

$$N + NO \longrightarrow N_2 + O \quad (16)$$

Several research groups have attempted to make use of this information.

The Exxon thermal $DeNO_x$ process is one of the successful methods to make use of these reactions (Lyon, 1976, 1987; Lyon and Hardy, 1986). It involves the three component reaction system NO, NH_3 and O_2. This combination was chosen because there is little reaction when only ammonia and oxygen are present. The NH_i radical therefore serves as a selective reducing reagent for NO since O_2 is at least two orders of magnitude more concentrated than NO. Attempts with other reducing reagents (H_2, CH_4, C_2H_6, CO) (Muzio et al, 1979) have shown these species to preferentially react with oxygen under the concentration conditions in question. While NH_3 does not react efficiently with NO directly (equation 27) it has been shown to be an adequate reducing reagent because it gives rise to the amine radicals, NH_i.

The Exxon thermal $DeNO_x$ process works well to nearly quantitatively reduce NO to N_2:

$$4NH_3 + 4\ NO + O_2 \longrightarrow 4N_2 + 6H_2O \quad (28)$$

in the temperature range of 1200-1400 K (Lyon, 1987). The presence of oxygen drives this reaction by producing radicals from ammonia:

$$O + NH_3 \longrightarrow OH + NH_2 \quad (29)$$

$$OH + NH_3 \longrightarrow H_2O + NH_2 \quad (30)$$

At temperatures below 1100 K, this reaction system will not proceed at all since not enough thermal energy is available to create the O radicals needed to initiate the reaction process. At temperatures above 1500 K on the other hand, there is enough thermal energy available to cause the oxidation of ammonia to NO:

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O \quad (31)$$

This defeats the purpose of reducing the NO concentration that was initially present to the point where one can end up with more NO than one started with.

This process is efficient, therefore, in only a very narrow temperature range. The range can be lowered, but not widened, by the addition of small amounts of hydrogen to the reaction system (Lyon, 1987). The narrow temperature range could pose problems for NO removal efficiency from the flue gases of a system where the temperature may not be easily well-controlled. For instance, for a power plant where the boilers are routinely turned on and off to accommodate loads, this might not be a convenient situation.

This NO removal process has been found to be greater than 90% efficient at the benchscale for a NH_3/NO ratio of approximately 2 (Muzio et al, 1979). The efficiency varies extensively with injection ratio. On the larger practical scale, the efficiency of removal is found to be in the range of 70-80% (Lyon, 1987).

In addition to the Exxon process, several other processes have been attempted to make use of the amine radical reactions in the flue gases. Other amines (CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$) have been found to give a selective reduction of NO, but not with as high an efficiency as ammonia (Muzio et al, 1979).

Urea, $(NH_2)_2CO$, has been used by spraying an aqueous solution of it into the flue gases (Mansour et al, 1987). It has proven successful in selectively reducing NO in the temperature range of 1000-1400 K, but the reaction is very temperature dependent. It was thought that this temperature dependence was due to the thermal decomposition of urea to produce two NH_2 radicals and one CO molecule, but the situation is now thought to be much more complicated than that. As a result, the mechanism is not sufficiently well-known to allow accurate modelling of the reaction system. The efficiency of this process is found to vary between 30-70% in the temperature range mentioned and for the optimum stoichiometry. One of the drawbacks to the use of urea is that CO is a byproduct of the decomposition of urea and as a result the concentration of CO in the flue gases is found to increase by 60-80 ppm.

Recently, attempts have been made to use cyanuric acid $(HOCN)_3$ as a precursor for the amine radicals (Perry and Siebers, 1986). Thermal decomposition of cyanuric acid produces isocyanic acid:

$$(HOCN)_3 + \text{heat} \longrightarrow 3HNCO \qquad (32)$$

which subsequently breaks down to produce amino radicals:

$$HNCO + heat \longrightarrow NH + CO \quad (33)$$

$$H + HNCO \longrightarrow NH_2 + CO \quad (34)$$

The amine radicals then proceed to reduce the NO in the flue gas. To date, this process has only been used on the benchscale but initial results have been promising. It has the advantage of proceeding at much lower temperatures than the other thermal processes. Reaction begins at 360°C and there is no temperature dependence of the efficiency to at least as high as 900°C. The reaction has also been shown to take place quantitatively at a near stoichiometric ratio of cyanuric acid to NO. Cyanuric acid has been injected in the gas phase or used as a heated bed of the solid.

All of these NO removal methods suffer from the same problems. A major complaint has been that the reagents are expensive. This complaint has mainly been voiced where ammonia is concerned. The other reagents mentioned here are much more expensive than ammonia. The thermal regulation problem is at least as bad for the urea process as it is for ammonia, especially if more NO is produced when the temperature is too high. The cyanuric acid process is not as temperature dependent, but it is not yet sufficiently well-studied to be of practical use.

The most serious problem to be considered when engineering this type of reactive system is the control of the ammonia slippage. That is, because the ammonia and urea processes operate at quite high ratios of reagent to NO, there is a tendency for some NH_3 to pass through the system unreacted (or recombined in the case of urea). When dealing with high sulfur coal combustion, SO_2 that remains in the flue gas (SO_2 control should precede NO_x control) will react with the ammonia to form $(NH_4)_2SO_4$ which tends to foul equipment (Mansour et al, 1987).

Despite these problems, for the proper operating environment these processes work very well for removal of NO confirming the usefulness of the amine radicals for NO destruction. It should be noted that most of these radical reaction processes tend to give the highest NO removal efficiencies for high initial concentrations of NO (Muzio et al, 1979). This is probably due to the fact that reaction with NO leads to additional radical formation to propagate the reaction chain. As a result, these removal processes are well-suited for coal-fired combustion except for the sulfur complications mentioned above.

5.2.2 Selective Catalytic Reduction

By far the most popular and the most successful flue gas NO_x control treatment has been selective catalytic reduction (SCR) (Kiovsky et al, 1980; Glass et al, 1983). This method involves the reduction of NO by ammonia over a heated catalyst bed

through which the flue gas flows. For optimized conditions the reduction occurs nearly quantitatively to give molecular nitrogen as the product.

This technique was developed in Japan where NO_x emissions are very strictly regulated and very efficient NO removal techniques are therefore required. Because of its success, the method has gained widespread acceptance in Germany and other European countries where NO_x control is becoming more tightly regulated (Reidich et al, 1986; Rentz, 1987). Because of the cost of this technique, and because the NO_x regulations are much more lenient, this process is not yet widely used in North America.

The SCR process, while microscopically much more complicated, is macroscopically described by a catalytic reaction of NH_3 and NO in the presence of oxygen which can be expressed as a series of overall reactions (Richards and Fox, 1980):

$$4NH_3 + 2NO_2 + O_2 \xrightarrow{cat} 3N_2 + 6H_2O \quad (35)$$

$$4NH_3 + 4NO + O_2 \xrightarrow{cat} 4N_2 + 6H_2O \quad (36)$$

$$6NO + 4NH_3 \xrightarrow{cat} 5N_2 + 6H_2O \quad (37)$$

$$6NO_2 + 8NH_3 \xrightarrow{cat} 7N_2 + 12H_2O \quad (38)$$

$$4NH_3 + 3O_2 \xrightarrow{cat} 2N_2 + 6H_2O \quad (39)$$

The actual stoichiometry and mechanisms that are responsible for the NO removal are dependent on composition of the catalyst, the characteristics of the catalyst support, the amount of oxygen available and many other parameters. Most of the catalysts that have been used are metal oxides on a variety of supports, although pure metal catalysts have also been used (Kiovsky et al, 1980). Successful metal oxides include CuO, Fe_2O_3, V_2O_5, CeO_2 and MnO_2. They have been impregnated on supports of zeolites, TiO_2, SiO_2 and Al_2O_3. The most successful and, therefore, the most popular catalyst has been V_2O_5 with TiO_2 favoured as the support material (Kiovsky et al, 1980; Takagi-Kawai et al, 1980; Bosch et al, 1986; Wong and Nobe, 1986) but Al_2O_3 has also commonly been used.

One can readily observe that this method of NO removal resembles the overall reaction of the thermal $DeNO_x$ procedure although the two detailed mechanisms are very different. The major effect of the catalyst on the overall reaction is to

allow the NO reduction to take place at a temperature of 300-450°C rather than the 1000°C required for the homogeneous reaction. As a result, heating of the flue gas and temperature control are not as much of a problem as with the homogeneous reduction. There are some problems at higher temperatures however. There is still a catalytic mechanism for oxidizing NH_3 to NO at higher temperatures (Kiovsky et al, 1980). A mechanism for converting NH_3 to N_2 by oxygen (equation 39) proceeds at a faster rate at higher T thereby depleting the NH_3 much more quickly than it can reduce NO. Some catalysts also seem to reduce NO to N_2O rather than N_2 if the temperature is not properly controlled (Kiovsky et al, 1980). As a result attention must still be paid to flue gas temperature to achieve the desired NO removal.

Although the overall reaction stoichiometries can be written as shown in equations 35-39, the actual mechanism which allows the NO removal to occur is far more complicated. A variety of mechanisms have been postulated for this removal depending on the catalytic system being used (Takagi et al, 1977; Inomata et al, 1980; Nalto et al, 1983; Wong and Nobe, 1986). All of these mechanisms involve a variety of adsorbed states going through a series of redox reactions. The participation of the catalyst appears to involve the metal in the metal oxide going through a series of oxidation and reduction reactions enabling the reduction of the NO, but ultimately leaving the catalyst in its original state.

It is strongly felt that the role of oxygen in the mechanism is to facilitate the adsorption of NO as NO_2 since NO is not itself readily adsorbed on the metal oxide surfaces (Takagi et al, 1977; Kiovsky et al, 1980). Although there is still some disagreement about this, infrared spectroscopic evidence of the adsorbed species seems to confirm this mechanism. An example of a postulated mechanism is:

$$NO + 1/2O_2 \rightarrow NO_{2(ad)} \quad (40)$$

$$NH_3 + \mathcal{F}\text{-}OH \rightarrow \mathcal{F}\text{-}O^- \text{---} NH_4^+ \quad (41)$$

$$NO_{2(ad)} + \mathcal{F}\text{-}O^- \text{---} NH_4^+ \rightarrow N_2 + 2H_2O + \mathcal{F}\text{-}O \quad (42)$$

This mechanism is speculative, but there is at least evidence that adsorbed states of this form must be involved in the removal of NO in catalytic systems. It is probable, however, that the detailed mechanisms can vary considerably between different types of catalysts and between various reaction conditions although the end result is the same.

In addition to the metal oxide catalytic systems, there are several examples of metal catalysts (eg, platinum, rhodium, etc) driving surface reactions between NO and CO (Muraki and Fujitani, 1986). Other reducing agents can also be used in

some of these systems. These catalysts are, however, more expensive than the metal oxide catalysts especially when considered for a practical large-scale operation.

For the metal oxide systems, the performance of the catalysts is really very good once the proper choice of catalyst and support has been made and the reaction conditions have been optimized. Most of the catalysts readily achieve 80% reduction of NO to N_2 with greater than 90% being attainable for optimum conditions on the small scale (Kiovsky et al, 1980).

There are, however, a great many problems associated with the use of SCR methods for coal-fired furnaces. The major problems involved are related to the naturally dirty environment and the large amounts of sulfur released with coal as a fuel (Richards and Fox, 1980; Glass et al, 1983). The dirty environment causes problems in that dust or fly ash and other unburned material found in the flue gases can plug the catalyst bed. This reduces access to the catalyst pores thereby reducing the effective surface area and the NO removal efficiency. Erosion of the catalyst bed is also a problem from this material. These problems are potentially solved by the installation of better filtering or other dust collection systems before the catalyst bed. It does, however, create an additional expense for these systems.

A far more serious problem arises from the fact that SO_2 will poison many of the catalyst beds thereby reducing their activity for NO reduction (Wong and Nobe, 1986). This can be alleviated by the proper choice of catalyst (V_2O_5 is resistant to SO_2 attack (Kiovsky et al, 1980)) and catalyst support (titania and silica supports are more resistant to SO_2 than is alumina (Takagi-Kawai et al, 1980)). Other problems may still occur in that some of the catalysts that are resistant to SO_2 (eg, V_2O_5) promote the oxidation of SO_2 to SO_3 in the presence of oxygen (Kiovsky et al, 1980):

$$SO_2 + 1/2O_2 \xrightarrow{cat} SO_3 \qquad (43)$$

The SO_3 may have the potential to create far more problems than the parent SO_2 in that it is highly corrosive and binds to the catalyst and support. As a result, many attempts are being made to find a catalyst-support system that is efficient for NO removal and that is resistant to SO_2 attack and will not form SO_3. One way to deal with this problem is to remove as much of the SO_2 as possible from the flue gas before it contacts the catalyst bed. This is done in many of the generating stations where SCR removal of NO is being successfully employed. The problem still exists to some extent since the efficiency of SO_2 removal processes is limited and some SO_2 is still emitted in the flue gases.

All of these problems amount to consideration of the fact that one must be willing to periodically replace or somehow recondition the catalyst bed when using the SCR technique for NO removal from the flue gases of coal-fired burners. This adds additional expense to these systems if one hopes to maintain the initial efficiency. Operating experience has shown the life of such catalysts to be from one to several years under optimum conditions at a slightly reduced NO removal efficiency (Reidich et al, 1986).

The same general problem as with other techniques that employ ammonia injection also exists for the SCR process. That is, if unreacted NH_3 is allowed to leave the catalytic reactor, it can react with SO_2 or SO_3 producing highly corrosive ammonium bisulfates that can damage air heaters and other equipment. This problem has been overcome by limiting ammonia slip to less than 5%, but this in turn causes the NO removal efficiency to be reduced to 60-70% due to the lower NH_3/NO injection ratio (Reidich et al, 1986).

A minor problem involves the proper choice of catalyst and support so that the operative mechanism does not promote the formation of N_2O rather than N_2. For example, Cr_2O_3 catalysts (Kiovsky et al, 1980) and SiO_2 supports (Takagi-Kawai et al, 1980) tend to promote N_2O formation probably by:

$$2NO_{(ad)} \longrightarrow N_2O + O_{(ad)} \qquad (44)$$

Other general problems relate to the cost of the initial setup for the catalytic reactor, the catalyst, better electrostatic precipitators and other equipment and the cost of the injected ammonia. Despite all of the setup and operation problems, proper engineering has resulted in many operating SCR processes in Japan and West Germany giving NO removal efficiencies of 70-80% (Reidich et al, 1986). As a result, it is evident that this is a very good method for NO removal when reliable high removal efficiencies are required.

5.2.3 Other Dry Flue Gas Treatments

A variety of other dry flue gas treatments have been attempted for NO removal (Ando et al, 1977; Glass et al, 1983), but for the most part they have shown only limited success. The dry alkali sorbent furnace injection technique that has been used for SO_2 removal has shown some effect on the NO concentration with a removal efficiency of 8-14% (Glass et al, 1983). The mechanism of this NO removal is not well understood and the hope for improvement in removal efficiency is small.

A copper oxide absorption process that has been used to achieve SO_2 removal at 400°C shows promise for NO removal as well (Ando et al, 1977). It follows a catalytic removal mechanism with NH_3 injection, but it operates at higher temperatures than most

SCR processes. It is useful in that it provides a possible joint SO_2/NO removal process, but it could suffer from the usual ammonia slip problems with SO_2 interaction and has not been developed very far.

An activated charcoal absorption process has also been used at 150°C for SO_2 removal. NO removal by this technique appears to be about 40% effective. The mechanism is not well understood. The catalytic reaction of NO with O_2 on carbon promotes the formation of NO_2 which is more readily absorbed by activated carbon, but then must be somehow washed off. Ammonia can also be injected to cause reduction by a catalytic process (Ando et al, 1977).

Bulk photochemical methods have also been attempted for NO removal (Richards and Fox, 1980). These methods attempt to take advantage of the usual atmospheric photochemical oxidation processes by controlling the oxidation to not go beyond NO_2 and then subsequently removing the NO_2. Such processes have met with very limited success and are very difficult to control because of the complexity of the reaction system.

The only other dry flue gas treatment that has really shown much promise for NO reduction to date is the Japanese electron beam process (Kawamura et al, 1979; Kawamura et al, 1980). It is a process by which simultaneous removal of up to 90% of both NO and SO_2 has been achieved.

The electron beam process is based on reactions of nitrogen, oxygen and hydroxyl radicals which are created by the radiolysis of O_2, N_2 and H_2O in the flue gas (Tokunaga et al, 1978):

$$O_2 + N_2 \sim\sim\sim> O_2^*, N_2^*, O_2^+, N_2^+, e^- \quad (45)$$

$$N_2^* + O_2 \longrightarrow N_2 + O_2^* \quad (46)$$

$$O_2^* \longrightarrow 2O \quad (47)$$

$$N_2^+ + O_2^+ \longrightarrow N_2 + O_2 \quad (48)$$

$$O_2^+ + e^- \longrightarrow 2O \quad (49)$$

$$H_2O \sim\sim> OH + H \quad (50)$$

The oxygen atoms and hydroxyl radicals which are in relatively high concentrations after radiolysis with ~1-2 MeV electron beams then proceed to oxidize NO:

$$2NO + 2OH \longrightarrow 2HNO_2 \longrightarrow NO_2 + NO + H_2O \quad (51)$$

$$NO + O \longrightarrow NO_2 \quad (52)$$

$$NO_2 + O \longrightarrow NO_3 \quad (53)$$

$$NO_3 + NO \longrightarrow 2NO_2 \quad (54)$$

$$NO_2 + OH \longrightarrow HNO_3 \quad (55)$$

SO_2 is also oxidized by a similar mechanism:

$$SO_2 + 2OH \longrightarrow H_2SO_4 \quad (56)$$

$$SO_2 + O \longrightarrow SO_3 \quad (57)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \quad (58)$$

These reactions proceed in a near quantitative fashion. The highly corrosive nitric and sulfuric acids present in the resulting mist are removed by the addition of ammonia to produce ammonium sulfates and ammonium nitrates which can be collected as a solid product. These species are potential fertilizer compounds and may therefore be sold to recoup part of the initial investment costs for this pollutant removal process.

This process has been shown to be capable of giving 90% removal for both NO and SO_2 and is operated at low temperatures (~100°C). The efficiency does not depend on residence time or dose rate, but only on the total dose and it actually appears to increase slightly for decreasing temperatures (Tokunaga et al, 1978; Kawamura et al, 1979).

There are, however, several problems with the use of this process including the corrosive acid gases which are present before the injection of ammonia. To help with this problem, it is possible to add the ammonia to the gases at the beginning of the radiolysis process without introducing additional problems. There have been some indications that NO can be produced rather than destroyed at very high radiolysis doses so it is important to keep the dose as low as needed to achieve efficient removal (Kawamura et al, 1980).

The two most serious drawbacks to this process have to do with the byproducts and the expense. The solid ammonium salt byproducts must be collected and removed from the flue gas. This is important to maintain a clean system and for the purpose of possibly selling the byproduct as a fertilizer. The collectors will add some expense to this process, but the major cost comes about because of the electron beam. A large number of electron guns are required to provide adequate coverage of the flue gas and as a result a great deal of energy (~3% of the power plant output) is needed to run this apparatus (Richards and Fox, 1980). The expense of the initial setup and the requirement of sufficient space for the installation can therefore cause significant drawbacks.

Despite the problems and the expense, the Japanese have been operating several pilot plants quite successfully for simultaneous NO and SO_2 removal. They have found that to achieve the most economical removal process, the efficiencies are reduced to ~80% for NO and ~75% for SO_2 (Kawamura et al, 1979).

6.0 RECOMMENDATIONS

The previous sections of this report have provided a comprehensive survey of the information that exists on the formation of NO in combustion processes and of the wide variety of methods that have been attempted to reduce the concentration of NO in the flue gases of thermal generating stations. It is evident that some of the processes work very well, but that there are problems associated with every one of them when they are used under practical conditions. Choosing which of the NO reduction methods to apply to a particular situation will therefore involve a series of compromises between efficiency, expense and complexity.

For the purpose of evaluating the available methods of NO reduction, one must first determine the extent of the reduction which is required and offset this with the estimated cost of the desired processes. It would certainly appear that where possible, one should make use of combustion modification procedures to reduce the amount of NO formed rather than trying to remove it later. Use of these techniques reduces the complication of adding additional equipment to the generating station. Commercial equipment is readily available for this mode of NO reduction and it is by far the cheapest and simplest method that can be used.

As has been pointed out earlier however, there are limitations to the use of combustion modification techniques. While the efficiency may prove adequate in the short term future, it is conceivable that regulations could be tightened to the point that combustion modification no longer removes enough NO to comply with the guidelines. The additional problem of the dependence of the removal efficiency on the coal burned makes meeting possible strict regulations with this action more of a problem. When considering the use of combustion modification in existing furnaces, there are the additional problems of lower efficiency in retrofit installations and the possible difficulties associated with accommodating new burners in an existing furnace configuration. This makes combustion modification a less attractive option for long term efficient NO_x emission reduction for existing facilities.

It appears therefore that while combustion modification seems the proper route for NO removal in the short term, one should be prepared to consider other possibilities for the more distant future. One must then be prepared to accept the fact that

flue gas treatment methods will necessarily cost considerably more than combustion modification.

If flue gas treatment procedures are to be undertaken, based on the technology available at this time, the method of selective catalytic reduction is likely the method of choice. This has been the case in Japan and Europe. The expense of flue gas treatment will obviously only be undertaken if the need for NO reduction is high, so it is wise to use the most efficient and most reliable method available. Other flue gas treatments either do not achieve the same efficiency (eg, wet processes), introduce significant complications and expense (eg, the electron beam process) or can experience considerable problems of reliability through the need for temperature control (the Exxon thermal DeNO$_x$ process). For these reasons, SCR appears to be the appropriate flue gas treatment procedure to follow despite the complications that can be involved.

In view of the cost of the procedures for extensive NO reduction and the problems that must be dealt with for situations involving SO_2 interference from the combustion of high sulfur coal, it would appear to be worthwhile to invest in research into new or improved methods for the future. The next section will outline possible areas of research where Ontario Hydro might make a contribution to the future of NO_x control.

7.0 POSSIBLE AREAS FOR RESEARCH

To date, research with regard to NO_x emission that has been carried out in this research section has dealt with the fate of NO_x species in the atmosphere. A tunable diode laser absorption spectrometer has been used to provide high sensitivity infrared absorption measurements of NO and NO_2 concentrations in the atmosphere. This technique has been used to make measurements of the dry deposition process of these species to a variety of surfaces. Such studies are valuable in understanding the effect of NO_x on the environment. There is room, however, for research directed more toward eliminating the NO_x problem at the source.

In view of the fact that there has been a large amount of high quality research carried out in the areas of most of the NO removal techniques described in this report, it is not likely that more research is going to produce significant improvements to the methods that are already available. This is particularly evident in the area of combustion modification where recent studies have produced only small gains in the NO reduction efficiency. It is unlikely that wet flue gas treatments are ever going to be simple processes which are efficient at removing NO. Improvements may be forthcoming in the area of selective catalytic reduction, particularly in the area of SO_2 interference with the catalyst itself. A research project in

this area is currently being conducted in this research group to gain a better understanding of the interaction between SO_2 removal and NO removal by SCR techniques. The Exxon thermal $DeNO_x$ process has also been extensively researched to the point where significant future gains are unlikely. There may be other gains to be made, however, in studying other applications of the radical reactions that are used in this process.

Many areas of NO removal by gas phase radical reactions have been pursued. The electron beam process is as good example of this, but it involves the use of oxidizing radicals (O, OH, HO_2) and therefore ends up producing a corrosive mixture that must be removed as a solid byproduct. The Exxon thermal $DeNO_x$ process and the other similar processes of this type described earlier, make use of reducing radical reactions which produce mostly N_2 as a harmless gaseous product. Reducing radicals are therefore much more useful in terms of removing NO in an uncomplicated fashion.

The radical reactions which may be of the most use for consideration of future research are those of the amino radicals (NH_i, i=0-2):

$$NH_2 + NO \longrightarrow N_2 + H_2O \qquad (14)$$

$$NH + NO \longrightarrow N_2 + OH \qquad (15)$$

$$N + NO \longrightarrow N_2 + O \qquad (16)$$

At least one of these reactions (reaction 14) has other product channels which may be accessible under some reaction conditions, but the indicated product channels are expected to be the dominant ones (Silver and Kalb, 1982; Whyte and Phillips, 1983). Much use has already been made of these radical reactions in the so-called thermal $DeNO_x$ processes (NH_3, urea, cyanuric acid). The problem with these processes has been the need to produce the radicals through some sort of thermal reaction process necessitating precise temperature control of the flue gas conditions to ensure that the reaction scheme follows the desired path. As a result, these reactions have been operated in the high temperature regime. It is known, however, that these reactions proceed at least as efficiently at room temperature (Morley, 1981; Whyte and Phillips, 1983; Harrison et al, 1986). In fact, it is suspected that these reactions have a negative temperature dependence. There is therefore no need to invoke high temperatures to take advantage of these NO reduction reactions, except from the point of view of forming the radicals in the first place.

It is therefore suggested that more research into ways of producing reducing radicals of this type and making use of their reactions to reduce NO in the stack gases might be a worthwhile effort. Problems existing with these radical

reactions include the radical formation and the fact that in a dense flue gas there is the possibility that the radicals can be quickly scavenged by other species before having the opportunity to react with NO. One must therefore give some consideration to the other species in the flue gas which may react with these radicals.

Of all of the species in the flue gases, N_2, O_2, CO_2 and H_2O are the most concentrated. The reactions of all of the above radical species with N_2 and CO_2 are highly endothermic processes and therefore need not be considered as a problem for the use of these radicals under low temperature conditions. Most of the reactions of NH_i (i=1-2) with H_2O are also endothermic. Reactions with oxygen are much more of a problem in view of the rate constants of these radicals with O_2 and with NO. These rate constants are shown in Table 2 for room temperature conditions. Rate constants for the oxidizing radicals are shown for comparison with an efficient reaction scheme.

It can be readily seen from this data that the rate constants for reaction of the amino radicals are larger than those for the oxidizing reactions that are already used in the electron beam process. It is also evident that the rate constants for reaction with O_2 are approximately three orders of magnitude less than those for reaction with NO. One must remember, however, that the concentration of O_2 in the flue gas is at least two orders of magnitude greater than the concentration of NO. By taking the NO concentration to be on the order of, but less than 1000 ppm and the concentration of oxygen as approximately 5%, one can calculate pseudo first order rate constants for the radical reactions with NO and O_2 assuming low radical concentrations:

$$k'_{NO} = k_{NO} [NO]$$

$$k'_{O2} = k_{O_2} [O_2]$$

The results of this calculation are shown in Table 3. These data indicate that each of these radicals is selective for reaction with NO under the concentration conditions given above. The rate of reaction with NO is largest with the NH radical, but the selectivity is highest for reaction with the nitrogen atom. This suggests that all of the radicals are useful for NO reduction, but that the choice of the most appropriate radical may vary with NO concentration. That is, for lower initial NO concentrations, the greater selectivity of the N atom may be required to achieve a more efficient removal of NO.

TABLE 2

RATE CONSTANTS OF SELECTED FREE RADICAL REACTIONS

REACTION	RATE CONSTANT	REFERENCE
	cm^3 $molecule^{-1}$ s^{-1} (300 K)	
$NH + NO \longrightarrow N_2 + OH$	5.78×10^{-11}	Harrison et al, 1986
$NH_2 + NO \longrightarrow N_2 + H_2O$	1.81×10^{-11}	Whyte & Phillips, 1983
$N + NO \longrightarrow N_2 + O$	3.4×10^{-11}	Lee et al, 1978
$OH + NO \xrightarrow{M} HONO$	1.3×10^{-11}	Baulch et al, 1980
$O + NO \xrightarrow{M} NO_2$	2.4×10^{-12}	Baulch et al, 1980
$HO_2 + NO \longrightarrow NO_2 + OH$	8.4×10^{-12}	Baulch et al, 1980
$NH + O_2 \longrightarrow NO + OH$	9.1×10^{-15}	Pagsberg et al, 1979
$NH_2 + O_2 \longrightarrow NO + H_2O$	$< 8 \times 10^{-15}$	Pagsberg et al, 1979
$N + O_2 \longrightarrow NO + O$	8.9×10^{-17}	Baulch et al, 1980
$OH + O_2 \longrightarrow HO_2 + O$	endothermic	Baulch et al, 1980
$O + O_2 + M \longrightarrow O_3 + M$	1.0×10^{-14}	Baulch et al, 1980
$HO_2 + O_2 \longrightarrow OH + O_3$	endothermic	Baulch et al, 1980

TABLE 3

COMPARISON OF RATE CONSTANTS FOR REACTIONS OF NO AND O_3 WITH VARIOUS FREE RADICALS AT FLUE GAS CONCENTRATION

RADICAL	k'_{NO} (s^{-1})	k'_{O2} (s^{-1})
NH	$<1.2 \times 10^{6}$	9.1×10^{3}
NH_2	$<3.6 \times 10^{5}$	$<8 \times 10^{3}$
N	$<6.8 \times 10^{5}$	8.9×10^{1}
OH	$<2.6 \times 10^{5}$	endothermic
O	$<4.8 \times 10^{4}$	1×10^{4}
HO_2	$<1.68 \times 10^{5}$	endothermic

Rates of recombination of the various radicals may also need to be considered as chain terminating steps in this reaction scheme. As long as the radical concentrations are reasonably low, however, the probability of recombination will be small compared to the NO reaction since the recombination reaction rates are on the order of the rates of reaction with NO (Whyte and Phillips, 1984; Harrison et al, 1986).

One must also be aware of the effects of the other products of the NO-radical reactions. In some cases they are oxidizing radicals. Again, as long as the radical concentrations are small, this should not be too much of a problem. In any event, the production of further radicals (O, OH) may help to keep the radical concentration high enough to promote chain reactions for further production of the NH_i radicals from the precursor molecules as seen in the ammonia thermal $DeNO_x$ process.

To consider some of these effects and to investigate the usefulness of these room temperature reactions for NO reduction, some further research into the formation and behaviour of these radical species in atmospheric pressure gases of flue gas com-

position is required. The method of optimum formation is not clear.

Thermal radical generation is not preferred because of the previous problems encountered in this with Exxon and other researchers. Photochemical generation of the radicals is also a problem in the flue gas since the penetration of the photons into the dense gas is poor and because coverage of the stack cross-section with photons is difficult. It would appear more efficient to attempt to generate the radical species outside the flue gas and inject them into the stack with the aid of high flows of unreactive gases (eg, N_2). Possible means of radical generation in this fashion are photochemical, microwave or rf discharge, chemical reaction, etc. A good way to examine some of these possibilities would be to investigate the behaviour of some of these radicals in the plasma torch. One of the problems which must be considered is the extent of penetration of the radicals into the flue gas before reaction and therefore the coverage density of injection sites that would be required. Proper engineering of a radical formation/injection system may solve this problem.

There is no guarantee that this research would lead to an economical NO removal process, but the selectivity and efficiency of these radical reactions appears promising. Research in the area described would help to answer some of these questions.

Further ideas for possible research involve the catalytic methods for NO removal. Since the problems with the SCR method of NO reduction mostly involve plugging or poisoning of the catalyst bed, it is suggested that a less problematic means of carrying out this type of process may be to disperse an aerosol of the catalytic material (eg, V_2O_5) into the flue gas and allow the catalytic reaction to take place on the particles. Such types of catalytic processes have been investigated for other reactions. To make such a process economical, a means of collecting and recycling the catalyst would be necessary.

All of these suggestions are merely speculative and will require some thought and experimentation to enable better evaluation. As for other areas of research, it has been suggested that perhaps more information can be gained about the combustion process of NO formation and destruction by the use of the tunable diode laser absorption spectrometer currently possessed by this research group to monitor pollutant and radical species concentrations. This may not be as promising as first thought.

It appears from the information contained in this report that much information is already available on these aspects of the combustion process. Information that is lacking involves the role of some of the radical species (OH, NH, etc) in the combustion process. While the tunable diode laser absorption technique is in theory capable of monitoring pollutant and

radical species in a flame (Hanson et al, 1980), it is not the method of choice for doing so (Crosley, 1980; McDonald, 1980). Because of the inherent insensitivity of the infrared absorption technique for detection, the TDL probe of the flame process must be carried out over a long absorption path. As a result, one must either be prepared to sacrifice detection sensitivity by reducing the pathlength or one must use a multipass technique. The latter option is going to cause the loss of spatial resolution in the flame - information which is required to tell where in the flame the critical reactions of NO formation or destruction are occurring.

The preferred methods of pollutant or radical detection in flames (or in other spatially related gas phase processes for that matter) involve the use of much higher-powered visible or ultraviolet pulsed lasers. The techniques of laser induced fluorescence (LIF) (Cottereau and Stepkowski, 1980; Grieser and Barnes, 1980; Morley, 1981; Fairchild et al, 1982; Copeland et al, 1984), and coherent anti-Stokes Raman spectroscopy (CARS) (Eckbreth, 1980) possess higher sensitivity and precise spatial and temporal resolution for the detection of such species, especially the transient radicals. Either of these techniques requires the use of a high-powered dye laser pumped by either a Nd:YAG or an excimer laser, systems not currently possessed by this research department. Resonance absorption techniques have been used for atom detection (N, O, H) (Thielen and Roth, 1984).

The research suggestions put forward in this section of the report are intended as suggestions of possible processes for NO reduction in the long term future (5-10 years) and are not meant as processes that will soon compete on a large scale with methods that are currently available. Research into these areas, however, may provide new information which will help in choosing a high efficiency NO reduction technique for long-term use.

8.0 CONCLUSIONS

A comprehensive survey of NO formation and destruction mechanisms in combustion processes has been carried out to gain a better understanding of methods currently used for reducing NO emissions from thermal generating stations. The currently used methods for NO reduction have also been surveyed and evaluated for their possible practical value for Ontario Hydro. Combustion modification has been determined to be the most practical short term NO reduction method for limited removal efficiency. If higher removals are desired at this time, the flue gas treatment technique of selective catalytic reduction is the most efficient and the most reliable.

Suggestions for areas of further research have been made. These studies may point the direction for longer term high efficiency NO removal processes.

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